

# EVALUATION OF NANOCLAY EXFOLIATION STRATEGIES FOR THERMOSET POLYIMIDE NANOCOMPOSITE SYSTEMS

Michael J. Gintert<sup>1</sup>, Sadhan C. Jana<sup>1</sup>, Sandi G. Miller<sup>2</sup>

<sup>1</sup>Department of Polymer Engineering, University of Akron, Akron, OH 44325-0301

<sup>2</sup>Polymers Branch, NASA Glenn Research Center, Cleveland, OH 44135

## Abstract

Prior works show exfoliated layered silicate reinforcement improves polymer composite properties. However, achieving full clay exfoliation in high performance thermoset polyimides remains a challenge. This study explores a new method of clay exfoliation, which includes clay intercalation by lower molecular weight PMR monomer under conditions of low and high shear and sonication, clay treatments by aliphatic and aromatic surfactants, and clay dispersion in primary, higher molecular weight PMR resin. Clay spacing, thermal, and mechanical properties were evaluated and compared with the best results available in literature for PMR polyimide systems.

## Introduction

Exfoliated nanoscale layered silicate particles have been seen to provide dramatic improvements in mechanical properties in polyamide systems [1]. Numerous studies have since attempted to achieve the same degree of reinforcement in an array of thermoset and thermoplastic polymer systems [2]. Layered silicate clays have been popular due to low cost, high surface area, and versatility of organic treatments available to make them compatible with a host of commercial polymer systems [3]. These clays are naturally available as tactoid structures consisting of several silicate layers stacked in crystalline lattice [4,5]. However, optimum reinforcement and improvement in thermal properties are obtained when tactoids are exfoliated into individual platelets [1-3,6-24].

A majority of prior work on polymer nanocomposites was focused on thermoplastic polymers [2,14-18] due to high levels of shear available in internal mixers and screw extruders during melt processing, which aid exfoliation of clay layers. On the other hand, most thermoset systems are cured under quiescent conditions and, unlike thermoplastic systems, shear forces of monomers are small and cannot be capitalized in achieving clay exfoliation. Nevertheless, an early model based on polarity-driven monomer diffusion into clay galleries was developed [3], which explained clay exfoliation in a number of epoxy-clay systems, although a universal understanding of the mechanisms of clay exfoliation is still lacking [9,19-24].

Park and Jana [23] took a unique approach in their work with epoxies. They intercalated clay galleries with aromatic epoxy and dispersed the mixture in a major phase aliphatic epoxy. In the process, a difference between intra- vs. extra-gallery crosslink density was created during curing. This resulted in much stronger elastic forces within the clay galleries, which effectively

pushed the clay layers apart against low viscous forces from the crosslinked aliphatic epoxy, thus causing exfoliation. Their observation can be summarized as follows. A faster increase of intra-gallery elastic forces compared to slower increase of extra-gallery viscous forces is conducive to clay layer exfoliation. The same methodology was applied in this work to produce clay nanocomposites of PMR-type polyimides.

PMR-15 polyimide resin [30] is one of the leading thermoset polymer resins for high performance aerospace applications. Several studies have been conducted in an attempt to further improve the mechanical and thermal properties by incorporating layered silicate clay into the PMR-15 matrix. To our knowledge no recipe exists for achieving full exfoliation of clay layers in PMR-15 composites [6-13, 31]. Researchers at NASA Langley Research Center (LRC) used high shear homogenizer and ultrasonication to produce clay dispersion in a solution of similar polyimide resins, which led to exfoliation and good clay dispersion in cured specimens as a result of high shear forces [6,12]. Other researchers used various organic treatments to promote favorable interactions between clay and polymer [3,9-11,25-28]. It was found that chemical structure of organic surfactant affects molecular orientation within clay galleries, thus directly influencing clay spacing. In addition, studies have shown that chemically reactive clay surfactants within the polymer matrix improve mechanical and thermal properties greater than nonfunctional surfactants. Other groups of investigators explored the effect of reduced cation exchange capacity (CEC) of clay surfaces, which reduces the amount of organic surfactant [11,29]. This research showed that clay dispersion in the polymer matrix improves as clay CEC decreases, due to the difference in intra-gallery molecular orientation.

## Experimental

### Materials

Two commercial nanoclays, Cloisite® 30-B (clay 1) and Cloisite® Na<sup>+</sup>, both from Southern Clay Products, were used. Two organic amines were used for clay treatments: N-[4(4-Aminobenzyl)phenyl]-5 norbornene-2,3-dicarboximide (APND), and dodecylamine (C12), both received from Aldrich. Nadic anhydride (NA) was acquired from TCI America, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) was purchased from Chriskev, and methylene dianiline (MDA) was obtained from Aldrich. Methanol and N-methyl pyrrolidinone (NMP) were used as solvents.

### Ion Exchange of Clay

Cloisite® Na<sup>+</sup> was ion exchanged with protonated forms of amines [3,25-26]. A 1:1 combination of APND:C12 was used to obtain higher clay layer separation in treated clay, as reported in an earlier work [32]. This clay will be referred to as clay 2 in the rest of the work. The properties of composites of clay 1 and clay 2 will be compared and contrasted later.

### Clay Intercalation

One gram each of PMR-5 (oligomer with MW 500) and organoclay (clay 1 and clay 2) were mixed in methanol and stirred for 18 hours before the clay was separated from the suspension by filtration and rinsed with methanol to remove residual PMR-5. The intercalated clay was dried in a vacuum oven at 75°C for 3 hours. Clay 1 and clay 2 intercalated with PMR-5 will be referred to as clay 1A and clay 2A, respectively. The suspensions of PMR-5 and clay particles in methanol were stirred using magnetic bar and optionally using high shear mixer and ultrasonicator. In one case, the suspension was stirred for 30 minutes using a stir bar, followed by ultrasonication at room temperature for 30 minutes and continued stirring by magnetic stirrer for 18 hours. In another case, the suspension was stirred only using a high shear cowled blade mixer for 4 hours at room temperature.

### Composite Synthesis

PMR-15 (oligomer with MW 1500) composites were synthesized by combining BTDE, NE, and MDA in the molar ratio of 2:2:3 in methanol, as per a standard procedure [30] and adding up to 5 wt% clay intercalated by PMR-5 to the monomer solution. A detailed procedure is presented elsewhere [32]. The composites thus produced will be designated by the type of clay used.

## Characterization

The values of storage modulus ( $G'$ ) and complex viscosity ( $\eta^*$ ) of crosslinking PMR-15 and PMR-5 resins were measured in ARES-M rheometer for curing temperatures between 50°C-330°C at a scan rate of 5°C/min. The oscillatory strain amplitude in a parallel plate setup was 1% and the frequency was maintained at 10 rad/sec. The extent of clay layer separation and exfoliation was investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Thermal and mechanical properties were determined using thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The temperatures at 5% weight loss ( $T_1$ ), and the maximum rate of weight loss ( $T_2$ ) were determined.

## Results and Discussion

### Imbalance of Molecular Forces During Curing

As Park and Jana [23] noted for clay-epoxy system, a difference in intra- vs. extra-gallery forces during crosslinking is key to achieving exfoliation (Figure 1). This was achieved in this work by intercalating the clay galleries with PMR-5 resin and dispersing the PMR 5-intercalated clay in PMR-15 resin before curing. Lower molecular weight PMR-5 resin produced more rapid increase of elastic forces measured by the values of  $G'$  during curing while the viscosity of the primary resin PMR-15 increased much more slowly (Figure 2).

Consequently, much higher degree clay exfoliation was produced in composites of clay 1A and clay 2A compared to those of clay 1 and clay 2 (Figure 3). Note that composites of clay 1 and clay 2 were produced by dispersing these clays in a solution of PMR-15 resin followed by curing; Figures 3 (a) and (c) reveal that clay particles remained in tactoid forms and did not exfoliate. In addition, the clay layer spacing from XRD was determined to be 1.5 nm. Composites of clay 1A and clay 2A were first intercalated with PMR-5 before dispersing in PMR-15. Figures 3 (b) and (d) show better exfoliation in these composites. These results established that the methodology adopted in this work based on prior clay intercalation by PMR-5 resins can lead to higher degree of exfoliation.

### Effect of Clay Organic Treatment

Recall that clay 1 is a commercial clay with an aliphatic quaternary ammonium ion while clay 2 contained an aromatic surfactant possessing the same norbornene end group as the PMR polyimide resin. In the latter case, the norbornene end group can potentially participate in crosslinking reactions with the PMR resin. Such reactive clay treatments have been reported to

greatly improve mechanical and thermal properties of composites [11,27].

In this study, the performance of clay 1 and clay 2 was compared in terms of degradation temperatures  $T_1$  and  $T_2$  measured using TGA. The values of  $T_1$  and  $T_2$  are shown in Table 1. The aromatic structure of organic treatment of clay 2 provides greater thermal stability than the aliphatic hydrocarbon in clay 1 – clay 2 lost 5% weight at 365°C, which is 85°C higher than that for clay 1, indicating that clay 2 is more suitable for PMR type resins especially in light of a high resin curing temperature of 315°C. It is also apparent from Table 1 that the organic treatment of clay 1 may undergo substantial degradation at high curing temperature of 315°C, which may lead to collapse of clay galleries and act as a deterrent to exfoliation.

Clay layer separation as determined from the peaks in XRD of composites of clay 1A and clay 2A (Figure 4) indicates that substantial thermal degradation of clay 1 occurred during resin curing at 315°C. This resulted in a collapse of clay galleries in composites of clay 1A. On the other hand, the clay layer separation increased in the case of clay 2A (Figure 4). Such increased clay layer separation, apart from higher thermal stability of clay 2 (Table 1), can be attributed to an increase in intra-gallery crosslinking density provided by the norbornene end group of organic treatment in clay 2.

### Effect of Mixing

Park and Jana [23] showed in epoxy nanocomposites that clay exfoliation starts at the surface layers and continues toward the center of the tactoid until all layers are exfoliated [23]. In view of this, we compared three techniques for dispersion of clay in resin solution where the objective was to obtain smallest possible tactoids before resins were subjected to curing. As a baseline method, a magnetic stir bar was used to disperse clay. In addition, a high intensity mixing blade and an ultrasonicator were used with expectation that better clay dispersion would be produced. Figure 5 presents TEM images of clay 2A in composites produced using these three mixing methods. It is evident that the magnetic stir bar provides sufficient energy for clay gallery intercalation by PMR-5 resin, however, the size of typical clay tactoids was large, e.g., many clay layers are seen stacked in the tactoid (Figure 5a). Clay dispersion using high-shear cowl blade, although was better than using stir bar, was not satisfactory, as large number of clay layers are still seen in tactoids (Figure 5b). On the other hand, sonication produced best results as the number of clay layers in stacks is significantly reduced (Figure 5c). Note that it is important to get as many layers separated as possible from the tactoids before the polymer reaches its gel point and ceases the molecular motion, which in turn prevents exfoliation.

It is also interesting to monitor the separation of clay layers in each stage of composite synthesis, including clay treatment, clay intercalation by PMR-5, B-staging, and finally resin curing. The XRD results of a typical experiment are presented in Figure 6. It is seen that spacing of clay 2A increases in each step. The clay peaks were not apparent after B-staging and curing, indicating that a majority of clay particles went through exfoliation during these steps. Researchers at NASA LRC have conducted similar work utilizing sonication and high shear mixing, and have shown promising results in regard to clay exfoliation and dispersion [6,11].

### Thermal and Mechanical Properties

Improvements in thermal properties were observed in composites of clay 1A and clay 2A compared to neat resin, as shown in Figure 7. The value of  $T_2$  increased by approximately 60°C for both composites of clay 1A and clay 2A over that of the neat resin. The value of  $T_1$  however did not improve much. It is apparent from Figure 7 that in the present system the improvement in thermo-oxidative stability was not dependent on clay treatment.

Addition of clay also improved stiffness as shown in Figure 8. An increase in modulus is observed for composites of clay 1A and clay 2A when compared with neat PMR-15. Clay 1A produces a greater increase than clay 2A. The difference in properties can be attributed to the differences in intra-gallery molecular orientation, as described by Campbell and Scheiman [28]. Several studies have found an increase in TOS; also increase in modulus by about 30% has been reported [6,8-12,28,33-35]. While these improvements are expected from clay reinforcement, other studies have shown that modulus values do not always increase significantly [31,33], and TOS is sometimes not affected by the inclusion of clay [13]. This implies that more work is needed to fully characterize the current system.

### Conclusions

The values of  $G'$  and  $\eta^*$  of the PMR system during curing present conditions favorable for clay layer separation, thus endorsing that intercalation of organoclay with PMR-5 before incorporation into PMR-15 is a viable approach to attain full exfoliation. The PMR-15 / clay composites produced in this study show that some individual layers are exfoliated while most are in an intercalated state, although in the form of tactoids with very small number of clay particles. Of the two organic treatments examined, a 1:1 mixture of APND and C12 performed better than Cloisite® 30B with regard to clay spacing and thermal properties, suggesting that aromatic reactive clay treatments are more beneficial than aliphatic modifiers for improvement of properties in PMR composites. In addition, it is shown that mixing plays a

key role in level of exfoliation, and sonication is an important step in clay tactoid breakup to enable exfoliation.

### Acknowledgements

Thanks to researchers at NASA GRC: Dan Schieman, Rick Rogers Bob Mattingly, David Hull, and Linda McCorkle. This work was funded by NASA GSRP Fellowship.

### References

- [1] K. Yano, et al. *J Polym Sci*, **31** 2493 (1993)
- [2] S. Ray and M. Okamoto. *Prog Polym Sci*, **28** 1539 (2003)
- [3] T. Pinnavaia, et al., *Chem. Mater*, **8** 1584 (1996)
- [4] R. Grim, *Clay Mineralogy*, 2nd Edn. McGraw-Hill, New York, (1968)
- [5] B. Theng, *Formation and Properties of Clay-Polymer Complexes*, Elsevier, New York, (1979)
- [6] D. Delozier, et al. *Polymer*, **43** 813 (2002)
- [7] M. Abdalla, et al. *Polymer* **43** 5887 (2002)
- [8] D. Dean, et al. *48th International SAMPE Symposium*, (May 11-15, 2003)
- [9] H. Tyan, et al. *Chem Mater*, **11** 1942 (1999)
- [10] H. Tyan, et al. *J Polym Sci*, **38** 2873 (2000)
- [11] D. Delozier, et al. *Polymer* **44** 2231 (2003)
- [12] C. Park, et al. *Polymer* **46** 9649 (2005)
- [13] S. Campbell, et al. *48th International SAMPE Symposium*, (May 11-15, 2003)
- [14] P. Messersmith and E. Giannelis. *J. Polym. Sci.* **33** 1047 (1995)
- [15] T. Pinnavaia, et al. *Applied Clay Science* **15** 11 (1999)
- [16] E. Giannelis, et al. *Chem. Mater.* **12** 2168 (2000)
- [17] J.L. Lee and C. Zeng. *Macromolecules* **34** 4098 (2001)
- [18] L. Doppers, et al. *Vibrational Spectroscopy* **35** 27 (2004)
- [19] T. Pinnavaia and T. Lan. *Chem. Mater.* **6** 573 (1994)
- [20] P. Messersmith and E. Giannelis. *Chem. Mater.* **6** 1719 (1994)
- [21] C. Ober, et al. *Polymer* **43** 4895 (2002)
- [22] L. Jiankun, et al. *J. Polym. Sci.* **39** 115 (2001)
- [23] J. Park and S. Jana. *Macromolecules*, **36** 2758 (2003)
- [24] J. Park and S. Jana. *Polymer*, **44** 2091 (2003)
- [25] T. Pinnavaia, et al. *ACS Symp. Ser.* **499** 145 (1992)
- [26] T. Lee, *Ph.D. Thesis*, Michigan State University (1992)
- [27] A. Pattanayak and S. Jana, *Polymer* **46** 3394 (2005)
- [28] S. Campbell and D. Scheiman, *High Performance Polymers* **March** 17 (2002)
- [29] S. Campbell and M. Liang. *High Perf. Polymers* **18** 71 (2006)
- [30] T. Serafini, et al. *J. Appl. Polym. Sci.* **1** 905 (1972)
- [31] M. Islam, et al. *Polym. Mater.* **84** 645 (2001)
- [32] M. Gintert, et al. *SPE ANTEC 2006*, Charlotte, NC. pp. 258 May 7-11, 2006.
- [33] M. Abdalla, et al. *Mat. Res. Soc. Symp. Proc.* **726** (2002)
- [34] K. Wang, et al. *Polymer Materials* **93** 213 (2005)
- [35] X. Hu. *Polym. Mater. Sci. & Eng.* **93** 209 (2005)

### Tables

Table 1. Thermal degradation temperatures of clays 1 and 2

	T <sub>1</sub>	T <sub>2</sub>
Clay 1	280°C	400°C
Clay 2	365°C	600°C

### Figures

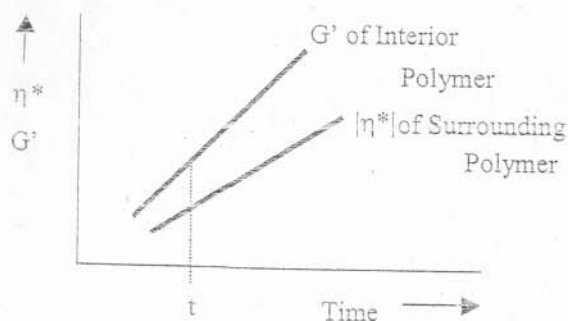


Figure 1. Relation between viscosity and modulus resulting in clay layer separation. [23,24]

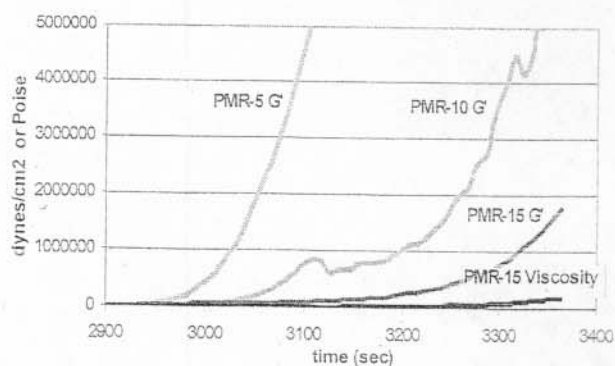


Figure 2. Rate of growth of  $G'$  and  $\eta^*$  values for varying molecular weight PMR polyimides.



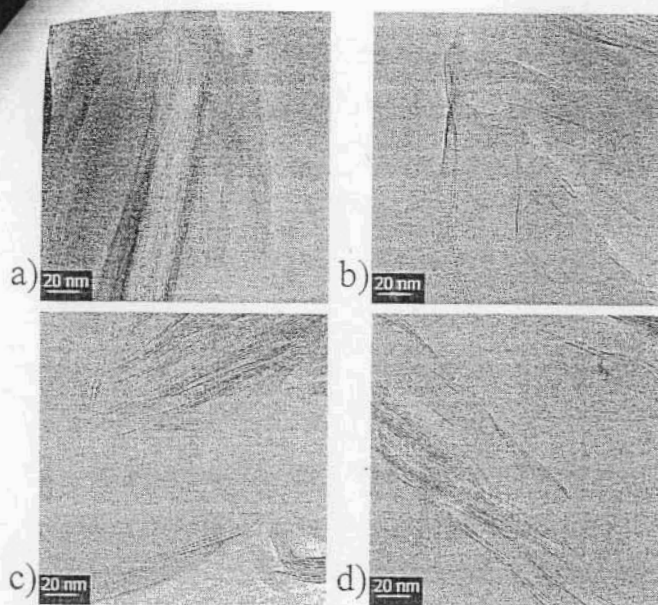


Figure 3. TEM images of composites of a) clay 1, b) clay 1A, c) clay 2, d) clay 2A

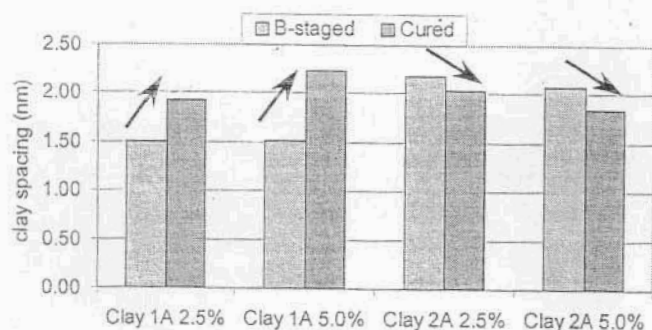


Figure 4. Clay layer separation before and after curing for composites of clay 1A and clay 2A, at 2.5wt% and 5.0wt% clay loading, prepared by stirring with magnetic stir bar.

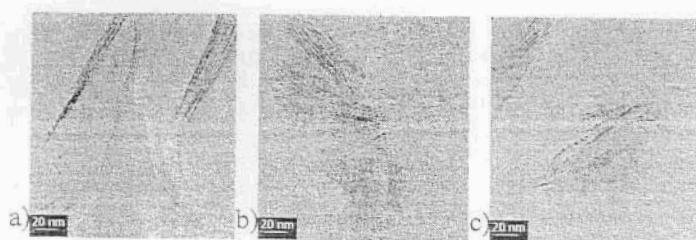


Figure 5. TEM of composites of clay 2A by various dispersion methods: a) stir bar, b) cowl blade, c) stir bar + ultrasonication

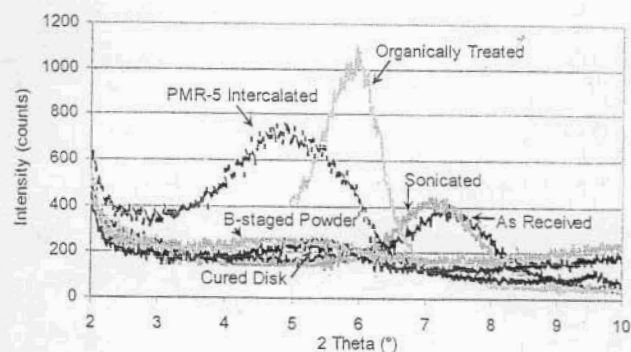


Figure 6. XRD plots showing clay 2A spacing at each stage of processing. (Clay dispersion was prepared by stirring with stir bar and ultrasonication.)

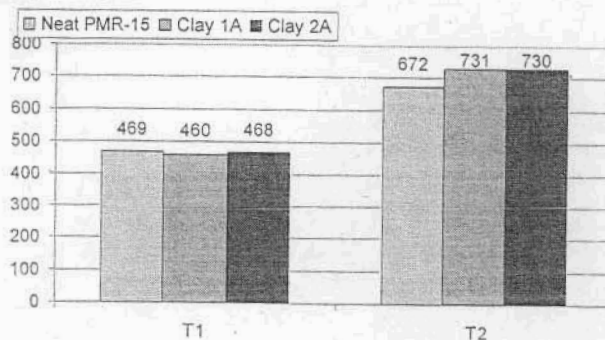


Figure 7.  $T_1$  and  $T_2$  values of neat PMR-15 and composites of clay 1A and clay 2A. (Clay dispersion was prepared by stirring with stir bar and ultrasonication.)

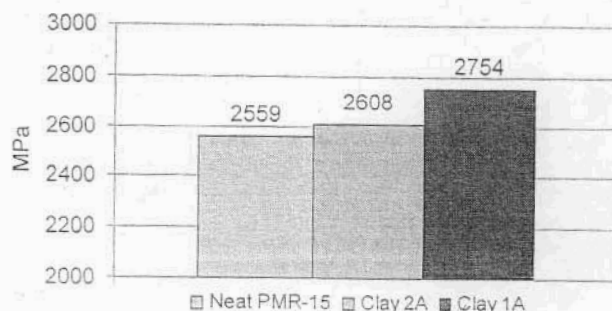


Figure 8.  $G'$  at 50°C by DMA for neat PMR-15 and composites of clay 1A and clay 2A. (Clay dispersion was prepared by stirring with stir bar and ultrasonication.)